FACULTY OF ENGINEERING AND ARCHITECTURE

Catalyst-assisted combined chemical looping: Super-dry reforming of CH_4

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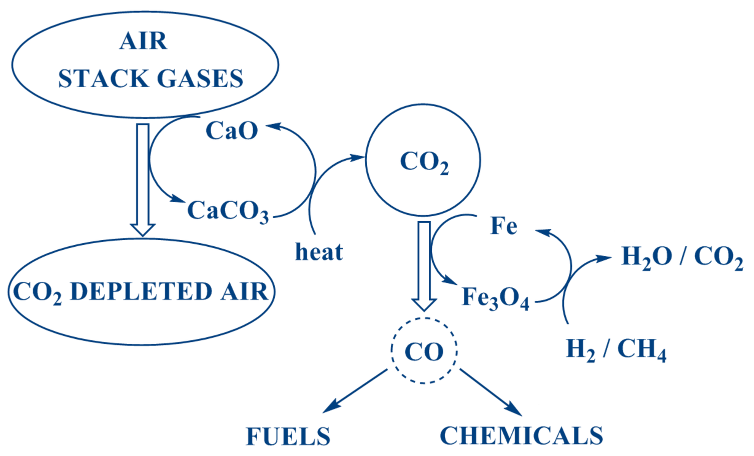
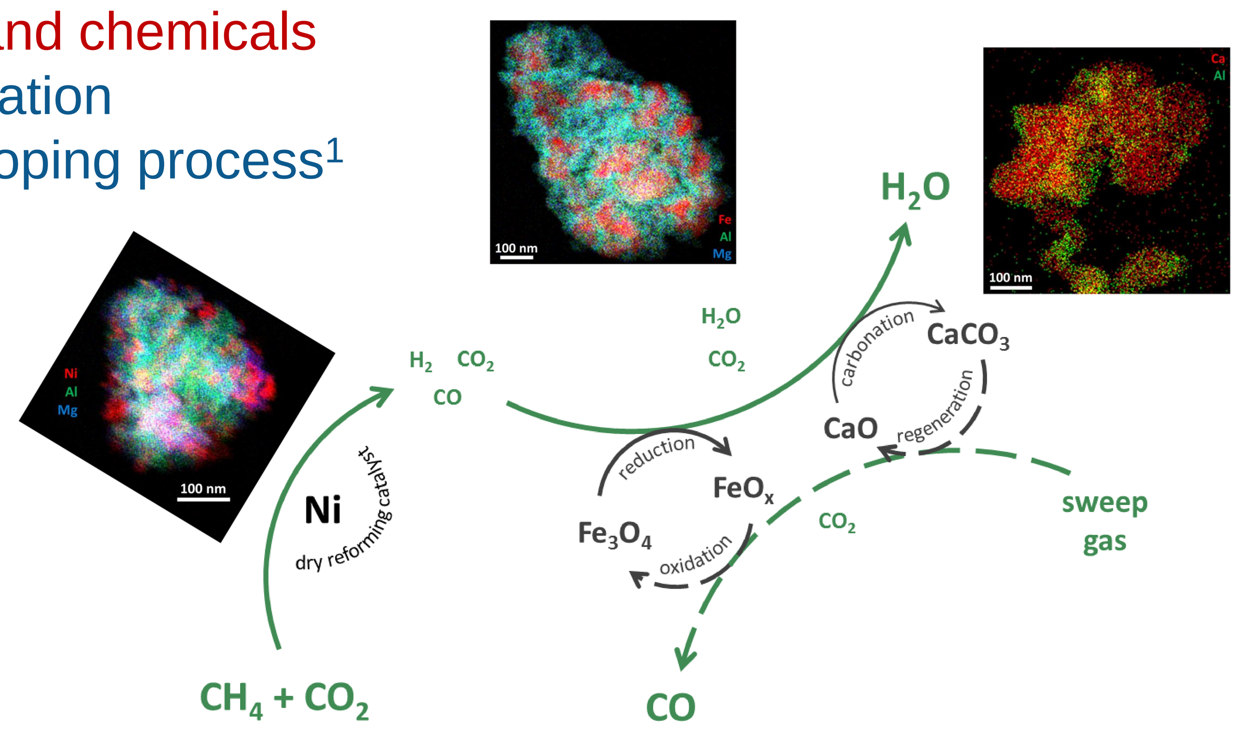
1 GENERAL INTRODUCTION

CO_2 as carbon source for fuels and chemicals

- ✓ CO_2 capture via metal carbonation
- ✓ CO_2 activation by chemical looping process[1]



Conventional chemical looping



Catalyst-assisted combined chemical looping

2 MATERIAL PREPARATION

Nickel oxide based material[2] (10w% **NiO**) with **$MgAl_2O_4$**: synthesized via incipient impregnation of $Ni(NO_3)_2$ on $MgAl_2O_4$ powder (prepared by co-precipitation of $Al(NO_3)_3.9H_2O$ and $Mg(NO_3)_2.6H_2O$ using NH_4OH as precipitation agent)

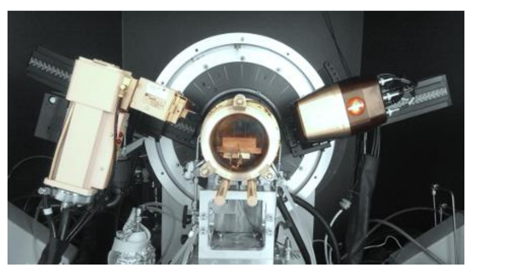
Calcium oxide based material (90w% **CaO**) with **Al_2O_3**: synthesized via wet physical mixing of CaO powder, $Al(NO_3)_3.9H_2O$ and citric acid as complexing

Iron oxide based material[3] (50w% **Fe_2O_3**) with **$MgAl_2O_4$**: synthesized via co-precipitation of $Fe(NO_3)_3.9H_2O$, $Al(NO_3)_3.9H_2O$ and $Mg(NO_3)_2.6H_2O$ using NH_4OH as precipitation agent

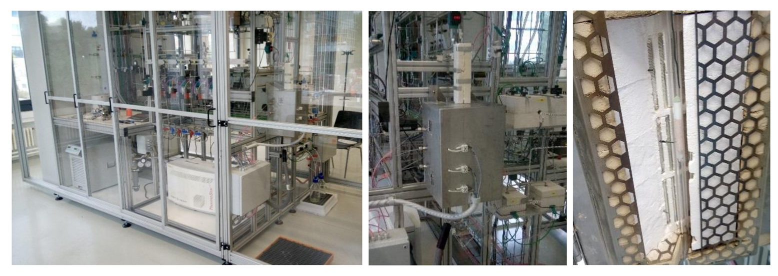
Advantages of CaO and Fe_2O_3: Earth abundant; Environmentally sound

3 METHODS

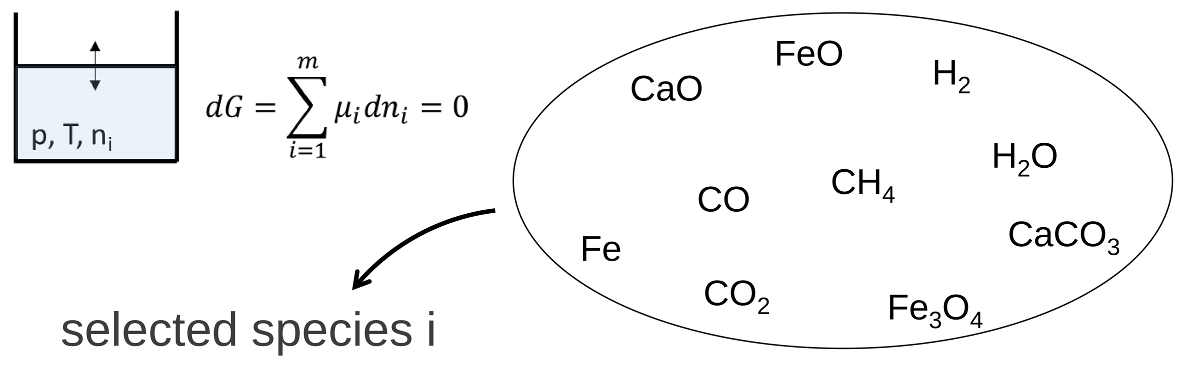
In situ XRD – Solid phase



Step response reactor – Gas phase



EkviCalc© [4] – Thermodynamics

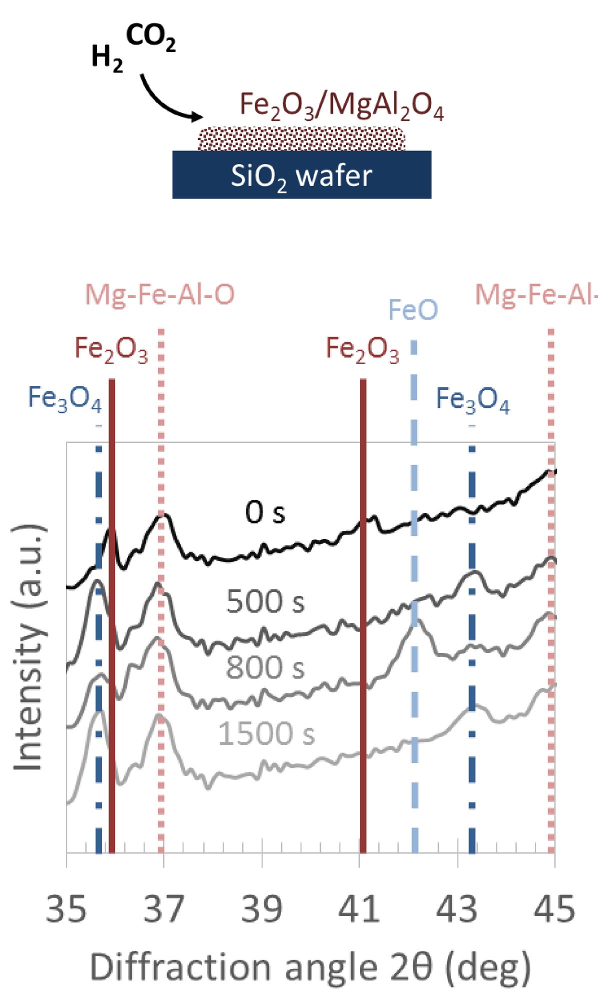


EkviCalc© contains database with reactions between selected species

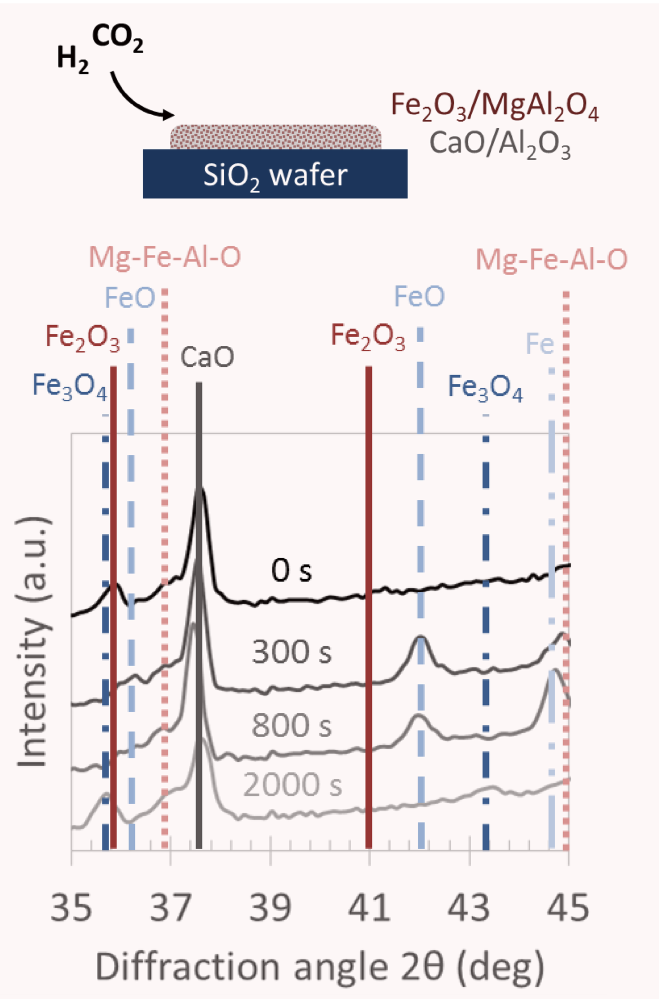
4 IMPROVED REDUCIBILITY OF IRON OXIDE

In situ XRD - Feed H_2:CO_2 mixture (1:1) at 1023 K (p=1 atm)

❖ Fe_3O_4 is slowly reduced: Fe_3O_4/FeO



$Fe_3O_4 \rightleftharpoons FeO$



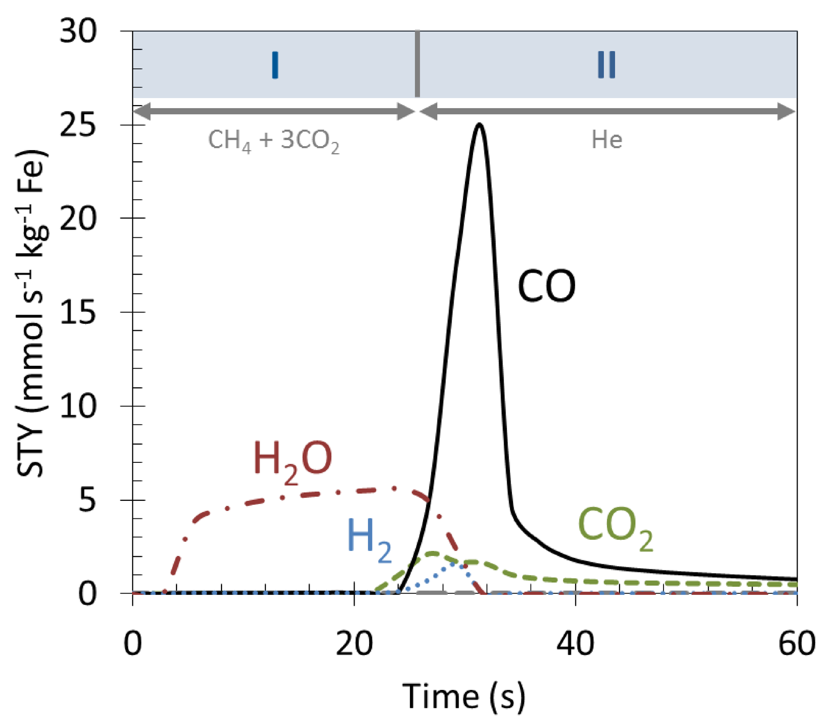
$Fe_3O_4 \longrightarrow FeO \rightleftharpoons Fe$

Addition of CaO (physical mixture)

- ✓ part of CO_2 can be extracted under the form of (surface) $CaCO_3$
- ✓ the reduction is faster and deeper: FeO/Fe

5 SUPER-DRY REFORMING OF CH_4

10Ni-$MgAl_2O_4$:50Fe_2O_3-$MgAl_2O_4$:90CaO-Al_2O_3 (1:3:6 mass ratio), 1023K, 1.5 bar



STEP I:

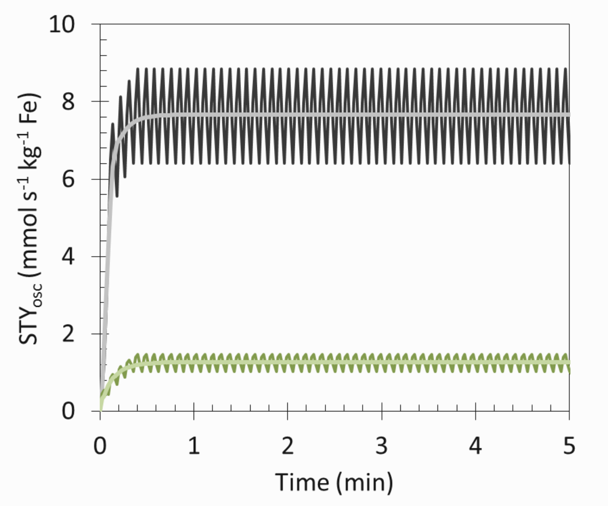
- ✓ High CH_4 conversion
- ✓ H_2O formation
- ✓ CO_2 capture

STEP II:

- ✓ CO_2 release
- ✓ CO formation

→ circumventing WGS reaction

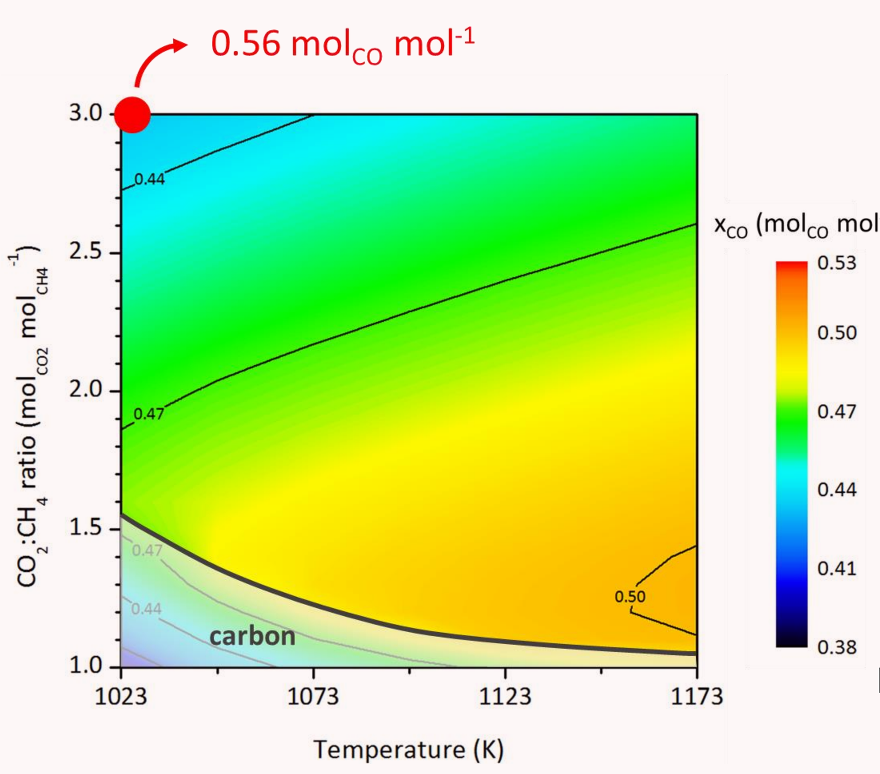
Dynamic simulation of multireactor configuration



Cyclic steady state:

- ✓ 7.5 $mmol_{CO}$ s^{-1} kg^{-1} Fe
- ✓ x_{CO} = 0.56

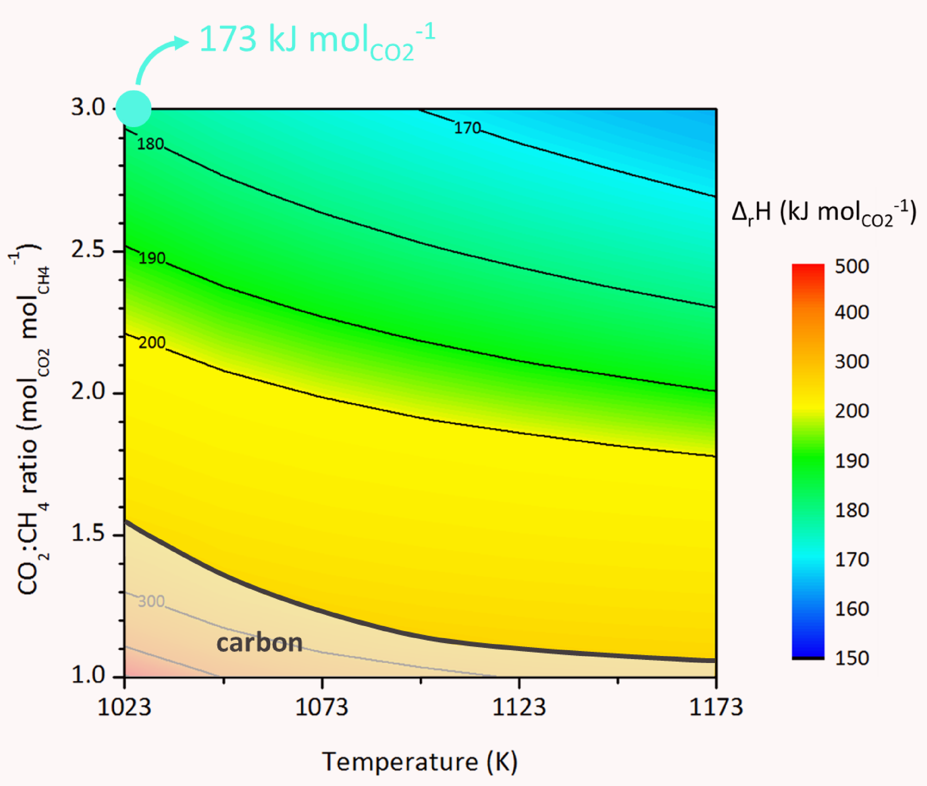
Comparison with thermodynamic equilibrium of methane dry reforming



higher CO purity

lower energy penalty

no carbon formation



6 CONCLUSIONS

- Super-dry reforming of CH_4 provides a promising method for CO_2 conversion
  - ✓ Dry reforming of CH_4 catalyzed by Ni catalyst
  - ✓ Presence of CaO strongly improves reducibility of Fe_3O_4
  - ✓ Efficient production of CO in relatively high purity due to inherent separation
  - ✓ Carbon formation thermodynamically unfavorable
- Combined with a renewable source of H_2, production of syngas in any ratio becomes possible due to intensified CO production process.

ACKNOWLEDGEMENT

This work was supported by the Long Term Structural Methusalem Funding of the Flemish Government, the Interuniversity Attraction Poles Programme, IAP7/5, Belgian State – Belgian Science Policy and the Fund for Scientific Research Flanders (FWO; project G004613N). L.C. Buelens acknowledges financial support from the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT Vlaanderen). The authors also thank Prof. Christophe Detavernier (Department of Solid State Sciences, Ghent University) for access to in situ XRD equipment.

REFERENCES

1. Galvita, V.V., et al., Industrial & Engineering Chemistry Research, 2013. **52** (25): p. 8416-8426.
2. Theofanidis, S.A., et al., ACS Catalysis, 2015. **5** (5): p. 3028-3039.
3. Dharanipragada, N.V.R.A., et al., Journal of Materials Chemistry A, 2015. **3**: p. 16251-16262.
4. Software package: BeN Systems, Örnsätra, S-74386 Bälinge, SWEDEN

International Congress on Catalysis (ICC 16), Beijing, China, July 3-8 2016